Status and future developments in the aqueous heavy element chemistry

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Recently, the status of the liquid-phase chemistry of the transactinide elements has been reviewed extensively in a number of reviews and book contributions [1-4]. In Table 1, an attempt is made to summarize the chemical systems studied with elements 104, 105, and 106, so far, and the pertinent references are given. The chemical techniques involved are briefly outlined. These include manual techniques, the multi-column technique (MCT), the automated rapid chromatography apparatus (ARCA), the on-line liquid-liquid extraction system SISAK in conjunction with liquid scintillation counting, and the automated ion-exchange separation apparatus coupled with the detection system for α-spectroscopy (AIDA). Critical comments [1] have been addressed to the results and conclusions presented in Refs. [8-12], and [14].

Technical developments are going on in several directions: The MCT has been coupled to the aerosol collection device ALOHA on which 2-s collection and dissolution cycles are performed so that the dissolved activity can be fed rapidly onto the sequence of chromatography columns in a quasi-continuous mode. The optimized conditions for on-line experiments with seaborgium are discussed in which Kd values on an anion exchange resin in 0.1 M HNO_3/5×10^{-3} M HF are planned to be measured via the long lived descendant of ^{265}Sg, 20-d ^{253}Es. It is also planned to reduce seaborgium to a lower oxidation state by contacting its aqueous solution with a hot aluminum surface and by distinguishing anionic seaborgium(VI) from cationic seaborgium (III) on a cation exchange column using the MCT.

Continuous efforts have been devoted to improvements of the on-line liquid-liquid extraction system SISAK coupled with liquid scintillation counting (LSC). Analog pulse-shape discrimination (PSD) has been used to reduce the β background in the α spectra by a factor of >1000. Without this technique, the β- and γ-induced background from activities produced in the target will interfere with the α spectrum to such an extent that it becomes useless. However, in the past, when feeding the He/KCl jet directly into the SISAK system, the PSD alone was insufficient to unequivocally identify transactinides with the SISAK - LSC system. Omtvedt et al. [17] have overcome this limitation by producing ^{257}Rf in the $^{208}Pb(^{50}Ti,1n)$ reaction, separating it in the Berkeley Gas-filled Separator (BGS), and transferring it to the gas jet using the Recoil Transfer Chamber (RTC). This was the first time that a transactinide was extracted and unequivocally identified by the SISAK - LSC system and also the first experiment to use preseparation in a transactinide chemistry investigation. Another improvement comes from the digital recording of the LSC pulses with a fast transient recorder and the pulse-shape analysis by an artificial neural network (PSD - NN) [29]. This has been proven to eliminate pileups to the extent that identification of transactinides even without preseparation becomes feasible. Its ability to recognize α-γ- and α-conversion-electron-coincidence summing which is known to cause shifted α energies may be used in the future to do nuclear spectroscopy [29].

Table 1.

Element	Isotope	Chemical technique	Chemical system studied	Ref.
104, rutherfordium	[261m]Rf	manual	Cation exchange/α-hydroxyisobutyrate	5
	[261m]Rf	manual	Aliquat 336/12 M HCl, 6 M HCl	6
	[261m]Rf	manual	Tri-isooctyl amine/12 M HCl	7
	[261m]Rf	manual	Thenoyltrifluoroacetone/0.05 - 0.24 M HCl	8
	[261m]Rf	manual	Tributyl phosphate/8 M - 12 M HCl	9
	[261m]Rf	manual	Tributyl phosphate/9 M - 12 M HBr	10
	[261m]Rf	manual	Co-ferrocyanide/<6 M HCl	11
	[261m]Rf	manual	Tri-isooctyl amine/0.4 M HF	12
	[261m]Rf	MCT	Anion exchange/0.2 M HF	13
	[261m]Rf	MCT	Anion exchange/0.27 M HF, 0.2 or 0.1 M HNO$_3$	14
	[261m]Rf	ARCA	Tributyl phosphate/6 M HCl	15
	[261m]Rf	ARCA	Cation exchange/0.1 M HNO$_3$, var. HF Anion exchange/0.1 M HNO$_3$, var. HF	16
	[257]Rf	SISAK	Dibutyl phosphoric acid/6 M HNO$_3$	17
	[261m]Rf	AIDA	Anion exchange/8 M HNO$_3$/4 M - 11.5 M HCl	18
	[263]Rf	manual	Cation exchange/α-hydroxyisobutyrate and Tributylphosphate/9 M HCl	19
105, dubnium	[262]Db	manual	Glass surfaces/fuming with HNO$_3$	20
	[262]Db	ARCA	Tri-isooctyl amine/12 M HCl, 0.02 M HF/10 M HCl, 0.025 M HF/4 M HCl, 0.02 M HF/0.5 M HCl, 0.015 M HF	21, 22
	[262]Db	ARCA	Diisobutyl carbinol/conc. HBr/6 M HCl, 0.0002 M HF/0.5 M HCl	23
	[262]Db, [263]Db	ARCA	Cation exchange/α-hydroxyisobutyrate	24, 25
	[262]Db	ARCA	Aliquat 336/10 M HCl/6 M HCl/6 M HNO$_3$, 0.015 M HF Aliquat 336/ 0.5 M HF/4 M HF/6 M HNO$_3$, 0.015 M HF	26
106, seaborgium	[265]Sg	ARCA	Cation exchange/ 0.1 M HNO$_3$, 5x10^{-4} M HF	27
	[265]Sg	ARCA	Cation exchange/0.1 M HNO$_3$	28

A new development in the field of liquid-liquid extraction is MicroSISAK based on the use of microsystem components [30]. Such a system provides separation times on the order of seconds at considerably reduced flow rates as compared to the conventional SISAK system. For mixing of the aqueous phase with the organic phase, a micro mixer is used where the phases are conducted through 2 mm long and 50 μm broad channels to a common outlet. The so-produced emulsion is subsequently separated in a filter apparatus on a filter membrane of 0.5 μm pore size. At a pressure differential of 10 mbar across the membrane and a flow rate of 0.5 ml min^{-1}, the aqueous phase is completely retained by

the hydrophobious membrane while the organic phase penetrates the filter. The goal is to eventually spray the organic phase onto a moving tape where it is evaporated to dryness and assayed for a activity by silicon detectors thus avoiding the drawbacks of LSC. In collaboration with the Institut für Mikrotechnik, Mainz, IMM, extraction yields are being optimized for flow rates below 0.1 ml min^{-1} [31].

For a future application to the spherical superheavy elements 112 and 114, the electrodeposition of these elements on certain electrode materials has been proposed [32]. It is well known that the electrochemical deposition of radionuclides in metallic form from solutions of extremely small concentrations depends strongly on the choice of the electrode material. The associated "underpotential" can deviate considerably from the Nernst potential. In a macroscopic model [32], the interaction between the microcomponent and the electrode material has been described by the partial molar adsorption enthalpy and -entropy. By combination with the thermodynamic description of the electrode process, a potential has been calculated that characterizes the process at 50% deposition. Model calculations for Ni-, Cu-, Pd-, Ag-, Pt-, and Au-electrodes and the microcomponents Hg, Tl, Pb, Bi, and Po have confirmed the decisive influence of the electrode material on the deposition potential. The experimental determination of "underpotentials" for some of these elements [33] is in qualitative agreements with the model predictions [32]. Plans for the application of this electrochemical technique to the spherical superheavy elements are presented.

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